

## Surface Contamination Analysis Technology Team Overview

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### Abstract

A team was established which consisted of representatives from NASA (Marshall Space Flight Center and Langley Research Center), Thiokol Corporation, the University of Alabama in Huntsville, AC Engineering, SAIC, Martin Marietta, and Aerojet. The team's purpose was to bring together the appropriate personnel to determine what surface inspection techniques were applicable to multi-program bonding surface cleanliness inspection. In order to identify appropriate techniques and their sensitivity to various contaminant families, calibration standards were developed. Producing standards included development of consistent low level contamination application techniques. Oxidation was also considered for effect on inspection equipment response. Ellipsometry was used for oxidation characterization. Verification testing was then accomplished to show selected inspection techniques could detect subject contaminants at levels found to be detrimental to critical bond systems of interest. Once feasibility of identified techniques was shown, selected techniques and instrumentation could then be incorporated into a multipurpose inspection head and integrated with a robot for critical surface inspection. Inspection techniques currently being evaluated include optically stimulated electron emission (OSEE); near infrared (NIR) spectroscopy utilizing fiber optics; Fourier transform infrared (FTIR) spectroscopy; and, ultraviolet (UV) fluorescence. Current plans are to demonstrate an integrated system in MSFC's Productivity Enhancement Complex within five years from initiation of this effort in 1992 assuming appropriate funding levels are maintained. This paper will give an overview of work accomplished by the team and future plans.

### Introduction

The Surface Contamination Analysis Technology team was established to address future surface cleanliness verification requirements for applicability in new manufacturing processes resulting from elimination of ozone depleting chemicals. Elimination of ozone depleting chemicals will effect shuttle hardware processing in two major areas. These areas are cleaning solvent elimination and replacement materials, i.e. primers, adhesives, and coatings. The Surface Contamination Analysis Technology team effort addresses the effect of losing solvents currently used in shuttle hardware manufacturing processes. Ozone depleting chemical elimination will effect currently used cleaning solvents, cleanliness verification solvents, and manufacturing materials containing targeted solvents. Ozone depleting chemicals identified in the shuttle program include for the largest part chlorinated solvents commonly used in cleaning processes and flight hardware cleanliness verification. Changes in processes and materials will effect future surface cleanliness verification requirements and their applicability in new manufacturing processes and inspections.

Replacement materials, which in all likelihood will be aqueous based and possibly more susceptible to contamination, when implemented may result in a bond system more sensitive to contamination. These concerns lead to the effort undertaken by the Surface Contamination Analysis Technology team. This effort, to identify alternate cleanliness verification techniques which can be applied both in laboratory and manufacturing environments, was initiated in 1992 in MSFC's Materials and Processes Laboratory. The goal was to develop a multi-purpose inspection system within five years. The new inspection system as conceived would consist of multiple techniques making up a single inspection head. The system would be used to detect, identify, and quantify contamination. Data attained would then be used to determine appropriate cleaning procedures.

## Concerns

### Cleaning Solvent Replacement Concerns

Cleaning solvent elimination will require replacement with alternate cleaning agents. The leading replacement candidates are alternate solvents, organic based cleaners, and aqueous based cleaners. Removal of contamination with candidate cleaners will depend on the type contaminant, its solubility / rinsability in the proposed cleaners, and cleaning process parameters. These new cleaning solutions may not remove contaminants as efficiently as solvents, i.e. residues may remain on surfaces after cleaning. If these residues prove detrimental to critical bondlines then new inspection techniques which are sensitive to low levels of contamination may be required for cleanliness verification prior to critical bonding operations.

### Cleanliness Verification Solvent Replacement Concerns

Current techniques for cleanliness verification such as water break and blacklight which have been used as acceptance tests in the shuttle program have limitations since they are subjective and qualitative techniques. If future cleaning processes leave detrimental residues which are not detectable with currently used inspection techniques more sensitive quantitative inspection techniques may be required. Non-volatile residue (NVR) analysis is a commonly used quantitative cleanliness verification method utilized in the Space Shuttle program. NVR analysis utilizes solvents (freon and 1,1,1 trichloroethane) on the elimination list. NVR sampling has been used for years in the shuttle program for hardware cleanliness acceptance. Liquid oxygen systems are evaluated for cleanliness with NVR which utilizes a laboratory flash evaporation of a sampling solvent to obtain a residue. NVR is quantitative but is dependant upon the sampling solvent being able to remove the expected contaminant. If NVR is detected the data gathered indicates the amount of material removed from the surface not what remains after NVR (flush or wipe) analysis. Residue remaining on the surface is of major concern. NVR analysis is used as a sampling technique and is impractical for 100 percent acceptance testing of surfaces of the magnitude found in solid rocket motor manufacturing. Since solvent NVR analysis cannot be accomplished in a real time manner there is a need for development of new, real time, quantitative cleanliness inspection techniques which can be applied to shuttle hardware manufacturing.

### Concerns with Replacement of Solvent Containing Production Materials

Adhesives and coatings which contain ozone depleting chemical components are used throughout the shuttle program. Materials which may require replacement in the near future include solvent based primers, adhesives, and coatings. Resulting formulation changes may change critical bondline response to contamination. If new materials implemented result in the bondline being more sensitive to contamination then new cleanliness inspection techniques may be necessary.

### Technical Approach

Concerns stated above lead to a search for cleanliness verification techniques which could detect a wide range of contaminants on critical surfaces. Residues may consist of organic and/or inorganic components depending on the cleaning solution and method used. Due to the range of possible contaminants and surfaces requiring inspection it is expected that a combination of techniques rather than a single technique would be used for cleanliness inspection. There is currently no available single technique capable of detecting organic and inorganic contaminants on various large surface areas in real time. Candidate techniques currently used in industry as well as those under development were considered. A plan for evaluating hardware bond surface characteristics such as substrate material type, surface roughness, and oxidation for metallic substrates, was developed. Inspection implementation parameters including inspection stand off distance, required inspection rate, environmental conditions, ease of operation, data interpretation, and direct applicability to existing manufacturing processes and facilities were considered. In order to

evaluate candidate inspection technique response to contamination both clean baseline standards and contamination standards had to be developed. The philosophy used in approaching standards development was first to determine what families of contaminants present in hardware processing environments. After contaminants were identified standards were developed to use in determining detection sensitivity and later calibration of the system. Techniques chosen had to detect contamination at levels which critical bond systems or surfaces were adversely effected. Development of processes for applying consistent low level contamination had to be undertaken. Processes and standards produced for evaluating and calibrating candidate inspection techniques were developed in parallel with some of the instrumentation characterization work.

### Substrate Characterization and Standards Development

Adequate surface contamination analysis requires proper characterization of the substrate to be inspected. This characterization includes determination of a baseline nominal surface resulting from the surface preparation process. The majority of effort has been with RSRM simulated surfaces, i.e. grit blasted steel and aluminum. Test panels were prepared with the same parameters as used on flight hardware as closely as possible with laboratory equipment. These panels were then used as a baseline noncontaminated data point to compare subsequent data to. Characterization of the inspection instrumentation was accomplished to verify instrument variability due to the substrate. One variable in the metallic substrates of interest was oxidation. Surface oxidation was considered for its effect on instrument detection of contamination since past experience with OSEE showed a sensitivity to surface oxidation. Aluminum surface reactivity was much higher than steel thus making it more of a challenge in characterization studies. Oxidation characterization testing was accomplished in an environmental chamber which varied temperature and relative humidity over a wide range. Test panels were prepared to simulate hardware flow then placed in the controlled environment and monitored over time. OSEE and NIR data were generated for substrate response with varying temperature and humidity levels. NIR characterization work showed a capability to differentiate between contamination and oxidation. This was an improvement over OSEE which showed a signal reduction from contamination and oxidation, i.e. OSEE could not differentiate between the two, making data evaluation difficult. This work was accomplished by UAH personnel under contract to Thiokol.<sup>(1)</sup> MSFC laboratories were used in accomplishment of these tasks.

Ellipsometry was performed on coupons exposed at various environmental conditions. Measurements were made to attempt to characterize various aluminum oxides which have been shown to effect OSEE signal from a substrate and may also effect other inspection techniques response. The problem encountered with aluminum studies has been the lack of optical property data on aluminum oxides. UAH has attempted to grow various oxides for ellipsometry characterization with some success. This work is continuing.

Substrate characterization work was paralleled with standards development for contamination response characterization and calibration. Common contaminants expected in the process had to be identified then characterized for their effect on instrument response. Major contamination sources identified included machining oils, hydraulic fluid, greases, silicone lubricants and release agents. After contaminants were identified they were grouped by chemical family. Contaminants within a family were assumed to have the same effect, i.e. degradation, on bonding. A single contaminant was then chosen from each family, normally the most prevalent in the manufacturing environment, since testing of all possible contaminants was impractical. Selected contaminants were then evaluated for ease of application and stability once applied to a substrate.

The majority of contaminants fell into two families, hydrocarbons and silicones. Some teflon release agents were used but silicones were used for the same purpose therefore silicones were assumed to simulate teflon materials adequately. Contaminants selected for standards included Conoco HD-2 grease, a tenacious heavy duty preservative grease used in RSRM production; CRC silicone oil, a silicone

lubricate; and Kaydol, a hydrocarbon mineral oil chosen to represent general hydrocarbon based materials. Kaydol was the only contaminant that presented problems with stability. The material appeared to migrate or disperse after a period of time. Paraffin wax was suggested as a contaminant since it would represent a hydrocarbon and be stable at room temperature. Application techniques were subsequently developed for chosen contaminants.

### **Contamination Application Techniques**

Thiokol modified an off the shelf machine for applying contaminants to test panels. The hardware manufactured by Sono-tek utilized an ultrasonic spray nozzle and conveyor track system for printed circuit board processing. A number of parameters were evaluated for effects on Sono-tek contaminant deposition. These parameters included track speed, solution concentration, pump volume or flow rate, nozzle orientation, and exhaust flow. Solution concentration was a major factor in obtaining consistent uniform coating with the Sono-tek hardware. Other application techniques evaluated included air brush application and immersion techniques. AC Engineering developed air brush application techniques. Contaminant level application was verified with gravimetric measurements made with aluminum witness foil sheets during both Sono-tek and air brush applications. An aluminum foil sheet was run through the Sono-tek equipment immediately before and after bonding panels to insure proper contaminant levels were being applied. Aluminum witness foils were exposed beside panels for air brush applications. NVR analyses of contaminated panels were done initially to verify the use of witness foils for deposition level verification. An FTIR microscope was used to characterize the contamination standards developed. Results of these tests are documented in an AC Engineering paper.<sup>(2)</sup> Verification techniques have shown Thiokol and AC Engineering have uniform and consistent procedures for application of contaminants at levels below five milligrams per square foot.

Ellipsometry was investigated also for detection and verification of contamination on various substrates. A problem encountered with ellipsometry was the lack of optical constants for various contaminants being evaluated. An effort is underway which will utilize a well defined substrate, silicone wafers, to which contaminant films will be applied then studied with ellipsometers in MSFC M&P laboratories. It is hoped this testing will allow determination of optical properties of common contaminant films which may be present on shuttle hardware prior to sensitive bonding operations. Results from this testing will feed data into other testing of various techniques which may prove useful.

After contamination application technique development, the next step was to determine critical bond system sensitivity to various contaminants. Bonding studies were conducted to determine at what contaminant level critical bond systems were degraded. Adhesive bond strength and failure modes were used to evaluate bond system performance or acceptability. High strength approaching the capability of the adhesive with a cohesive failure mode were desired. Cohesive failure is considered as failure within the adhesive or within the material being bonded to the substrate of interest. Adhesive failure, failure at the adhesive/substrate interface, indicates problems generally resulting from surface preparation, processing, or contamination. Bonding tests showed epoxy bondlines were sensitive to certain contaminants at levels below five milligrams per square foot of surface area. RSRM vulcanized bonding for insulation applications was generally an order of magnitude less sensitive. AC Engineering's efforts in support of the Surface Contamination Analysis Technology team work are detailed in "Standardization of Surface Contamination Analysis Systems".<sup>(2)</sup>

### **Technique Investigation**

Techniques being evaluated for incorporation into an inspection system include those which analyze surfaces over a wide wavelength range. Techniques currently being evaluated include optically stimulated electron emission (OSEE), near infrared (NIR) fiber optic spectroscopy, diffuse reflectance Fourier transform infrared (FTIR) spectroscopy, and ultraviolet (UV) fluorescence. Capability determination for

most of these contamination detection techniques is currently underway. A combination of techniques may be useful in surface cleanliness verification as a replacement for currently used inspections including blacklight, water break, and nonvolatile residue sampling. Following is a brief description of each of the previously mentioned inspection techniques.

## OSEE

OSEE is currently used in the RSRM program for case cleanliness inspection prior to primer / adhesive application for insulation bonding and nozzle housing inspection prior to epoxy adhesive bonding. This non-contact technique is sensitive to low level contamination on steel and aluminum substrates. Initially OSEE was implemented to detect residual grease on the internal D6AC steel motor case after vapor degreasing. The technique was sensitive to grease levels below 10 milligrams per square foot of surface area which was below the acceptance limit of 25 milligrams per square foot set at that time. OSEE was the only technique available at the time which could yield real time data on surface cleanliness of large motor case surface areas prior to subsequent processing. Other techniques were available for quantification of grease / contamination levels but data was not available in real time. OSEE detects changes in surface chemistry but can not identify what the source of change is. A complementary technique for contaminant identification would be useful when OSEE indicated a surface contaminant. A background and overview of OSEE application in RSRM manufacturing is detailed by Mattes.<sup>(3)</sup>

## OSEE Third Generation Development

The original OSEE equipment implemented in RSRM manufacturing had electronics and some quality control problems. Thiokol and the OSEE equipment manufacturer, Photo Acoustic Technologies, developed a second generation, industrial hardened, OSEE system which solved some of the problems with the initial design. Langley Research Center (LaRC) became interested in the technique and evaluated the original OSEE system design. A characterization of the physics of OSEE was undertaken at LaRC under the direction of Dr. W. T. Yost. Dr. Chris Welch of the College of William and Mary conducted characterization tests on the system. Deficiencies in the system were identified and proposals for improvements made in LaRC's evaluation report.<sup>(4)</sup> A third generation OSEE system as it was referred to was designed considering LaRC's identified improvements and MSFC Surface Contamination Analysis Technology team suggestions from equipment use history. A third generation six inch sensor system was fabricated by LaRC from funding provided through NASA headquarters Code QW.<sup>(5)</sup> Preliminary testing of the OSEE III system at MSFC shows improved stability over the current system, much quicker response time, and less effect from environmental fluctuations due to the argon purge implemented as part of the redesign. The LaRC team has applied for patents on electronic improvements made in the OSEE equipment.

## IR Spectroscopy Techniques

Spectroscopic techniques were evaluated for feasibility to manufacturing on-line applications. The Surface Contamination Analysis Technology team members experienced with spectroscopic techniques and their application to process monitoring included the University of Alabama in Huntsville (UAH) In-line Process Control Laboratory. A Guided Wave 260 spectrometer with fiber optic probes was used in MSFC's laboratories to characterize RSRM substrates of interest, D6AC steel and 7075 aluminum. Tests were conducted to evaluate oxidation and contamination on these substrates. Results showed NIR use was feasible for detecting contaminants on these substrates and differentiating between contamination and oxidation after applying appropriate data analysis software. Details of this testing are discussed in "Study of Surfaces Using Near Infrared Optical Fiber Spectrometry".<sup>(6)</sup>

A joint effort between Thiokol and TMA Technologies resulted in the development of a diffuse reflectance infrared instrument, the SurfMap IR, which was evaluated by Thiokol personnel in MSFC

laboratories. The instrument was proficient in detecting hydrocarbon contamination on aluminum and steel substrates. Additional information can be found in "Cleanliness Evaluation of Rough Surfaces with Diffuse IR Reflectance".<sup>(7)</sup>

Interest in a portable FTIR system with resolution and speed for real time inspection was expressed in the Surface Contamination Analysis Technology technical interchange meeting held last year. Discussions with Dr. G.L. Powell from Martin Marietta's Oak Ridge Y-12 plant led to a procurement request for a state-of-the-art portable FTIR system applicable to manufacturing line surface inspection. Specifications calling for compact size (one cubic foot) and low weight (less than 15 pounds) were written with robotic applications in mind. Proposals have been submitted and evaluations are currently underway. Advancements in microelectronics and computational software with increased data processing speed have made these type systems a possibility for real time surface inspection. Plans are to procure the equipment and test it in MSFC's Productivity Enhancement Complex robotic test bed within the next year.

#### Fluorescence Techniques

An ultraviolet (UV) fluorescence technique initially funded through a Small Business Innovative Research phase I contract with LaRC was transferred to MSFC and later approved for phase II funding. Phase I testing showed this technique was capable of detecting low levels, less than 10 milligrams per square foot, of contamination on different substrates common in the shuttle program, e.g. steel, aluminum, and insulation. The technique was also demonstrated as being capable of inspecting hardware from standoff distances on the order of feet while scanning as much as 15 square feet per frame. Feasibility for inspecting large surface areas in a short period of time would be a major advantage of using this system. Details on this inspection technique are available in "Contamination Detection NDE for Cleaning Process Inspection".<sup>(8)</sup>

#### MSFC Productivity Enhancement Complex Test Bed

MSFC, Materials and Processes laboratory has a unique facility for evaluation / development of manufacturing processes and equipment. The Productivity Enhancement Complex (PEC) located in MSFC's building 4707 contains robotic workcells and equipment for accomplishing a wide range of full scale manufacturing processes. A PEC CimCorp gantry robot will be utilized as a test bed for inspection system evaluation. The same robot was used previously to test a three axis OSEE end effector designed by Martin Marietta for RSRM nozzle hardware inspection.

OSEE III, fiber optic NIR, SurfMap diffuse IR, and ultraviolet fluorescence systems are currently under development for in-process manufacturing applications. These systems should be available for testing in the PEC test bed by mid 1995. Other techniques will be evaluated as they become available.

#### Conclusion

Techniques being evaluated as part of the Surface Contamination Analysis Technology team effort appear promising for applicability to shuttle hardware inspection. Availability of a technique which will allow quick inspection of large surface areas consistent with solid rocket motor bonding surfaces appears feasible. Contamination identified in an initial scan could then be evaluated with a more sensitive spectroscopic technique which could identify species present. This information would in turn allow a cleaning procedure to be defined. Applications for this technology exist throughout the shuttle program as well as in commercial applications resulting from technology transfer.

#### Acknowledgements

Surface Contamination Analysis Technology team members

## References

1. Workman, G. L., C. Hughes, W.F. Arendale, In-line Surface Chemistry Analysis, Final report to Thiokol Corporation, Contract 3MR029, September 1993.
2. Boothe, R. E., Standardization of Surface Contamination Analysis Systems, Aerospace Environmental Technology Conference Proceedings, August 10 - 11, 1994.
3. Mattes, R. A., Background and History of OSEE in RSRM Manufacturing, Aerospace Environmental Technology Conference Proceedings, August 10 - 11, 1994.
4. Yost, W. T., C.S. Welch, N. Abedin, OSEE Science Base, Final Report, Langley Research Center
5. Yost, W.T., et al, Design and Performance Considerations for the Third Generation OSEE Probe and Associated Electronics, Aerospace Environmental Technology Conference Proceedings, August 10 - 11, 1994.
6. Workman, G.L., W.A. Arendale, C.Hughes, Study of Surfaces Using Near Infrared Optical Fiber Spectroscopy, Aerospace Environmental Technology Conference Proceedings, August 10 - 11, 1994.
7. Pearson, L.H., B.D. Swimley, Cleanliness Evaluation of Rough Surfaces with Diffuse IR Reflectance, Aerospace Environmental Technology Conference Proceedings, August 10 - 11, 1994.
8. Marinelli, W., D. Blair, V. DiCristina, Contamination Detection NDE for Cleaning Process Inspection, Aerospace Environmental Technology Conference Proceedings, August 10 - 11, 1994.

